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High efficiency SiO₂–TiO₂ hybrid sol-gel antireflective coating for infrared applications

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Sol-gel derived antireflective thin films were created for chalcogenide glass substrates in the 1.5–5 μm wavelength range of infrared region. Presented herein is a preparation and characterization of the hybrid sol-gel created including particle size, refractive index, pH, and Fourier transform infrared FTIR transmission spectra. It is shown that an increase of not less than 8% and up to 25.1% transmission is achieved using sol-gel derived antireflective coatings. © 2006 American Vacuum Society. [DOI: 10.1116/1.2210007]

I. INTRODUCTION

For many years, antireflective coatings have been successfully created from sol-gel derived thin films. In recent years, chalcogenide glass has emerged as a useful material in applications such as optical switching, biomedical, and thermal imaging.^{1–7}

Most studies found in literature are concerned only with the midinfrared transmission of chalcogenide glass. In many cases, this is the most important range and also the best range for transmission properties. Lacking, though, is a low cost method of improving the transmission characteristics of chalcogenide glass in the low-infrared range. Chalcogenide glasses are made up of group IV–VI elements, group II–VI elements, or other combinations thereof and has semiconducting properties.^{8,9} Of interest is their transmission throughout the infrared region and the non-linear refractive index.^{10,11} Further, such materials have high chemical stability.¹¹ Common applications of this unique glass substance include night vision systems and thermal imaging. Both applications exploit the excellent transmission of the chalcogenide glass throughout the infrared region of light.¹²

The increase of transmission is because of the reduction of light lost due to reflection. To make an antireflective layer for one specific wavelength requires that the layer have a certain thickness and refractive index. The coating must follow the formula

$$n_{\text{coating}} = (n_{\text{substrate}})^{1/2}$$

for the coating refractive index. The proper combination of these creates out of phase reflections that rebound from the medium. In general, a single quarter-wavelength coating with a refractive index that is the square root of the substrate is used to achieve full transmission.¹³ Multilayer coatings

can be used to expand the properties of a single layer, among many layers. Using this theory, many layers of different thicknesses and refractive indices are layered to allow for different wavelengths.

Current antireflective coating techniques are limited to two broad categories. The first involves the creation of a coating that has very high transmission for a certain wavelength of light. This technique is very useful for applications that use particular wavelengths of light, as in lasers. The second type is termed broadband coatings. Some of the techniques used to create these functional coatings include multilayer coatings (MLC), submicron structures, and sol-gel derived antireflective (AR) coatings.

The multilayer coatings are extremely effective for transmission across a large range of wavelengths. The drawbacks of multilayer techniques are their intrinsic complicated nature. The challenge is to maintain coating thickness while minimizing defects. Further, multilayer coatings can be mechanically unsound when compared to singular layers, given similar materials and process parameters.¹⁴

Finally, sol-gel derived AR coatings, being the easiest to apply, show the most potential in “broadband” applications. Unlike MLCs, single layer sol-gel coatings are very mechanically sound and are simple to create with minimal defects. Also, similarly to submicron structured AR techniques, sol-gel derived AR coatings can be created in such a way to use submicron particles to affect both the refractive index and the light scattering within the coating.⁵

One of the most common coating materials used for antireflective properties is silica. The hybrid combination of silica and titania creates the refractive index we wanted. However, other material combinations can be used to achieve similar refractive index values while still using the mechanically strong sol-gel thin film. Examples of alternative materials that use a particular chalcogenide glass as a thin film are As₂S₃ or Ge₄₅Se₅₅.¹⁵ These unique materials have very low

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absorbance in the infrared region and combinations of these materials can be used to alter the refractive index through a wide range. Similar systems can be developed that include the use of many different coating materials to achieve the desired refractive gradient, such as an As₂Se₃/BaF₂/air system, which depends on the densification of the film through heat treatments for mechanical stability.¹⁵ Although such a coating is feasible for the appropriate optical qualities, the strength of the film cannot be fully achieved without subsequent heat treatments used to densify, reduce porosity, and create stronger linkage between layers.¹⁶ Due to the nature of the chalcogenide glass substrates used in the research presented herein, a heat treatment can only be applied with extremely small temperature increases. Even with a substantial time period used to raise the temperature, the maximum temperature allowed before a change in structure is 100 °C. This implies the need for a coating system specifically designed to be fully operational without a heat treatment. Because of the aforementioned mechanical stability of a single layer system versus a multilayer system, the development of a coating with the correct optical properties within a single coating layer was necessary. Further, the intention to create a low cost, efficient, and easily reproducible method was paramount.

II. EXPERIMENT

A. Preparation of the sols

The hybrid sol-gel is created in a multiple step process combining the two different components after aging (Fig. 1). A silica sol-gel is created with equal parts of tetraethylorthosilicate (TEOS) (+99%) and ethanol (anhydrous, 85%). The sol reaction utilizes nitric acid for hydrolysis and de-ionized (DI) water, added dropwise, for water condensation. The sol is then covered, to prevent evaporation, and left for aging for a day.

The second part of the hybrid sol-gel is the titania. Components of the titania film include titanium (IV) isopropoxide (97%), 2-propanol (Grade GC, 99.7%), and DI water. The isopropoxide is added to the propanol to avoid evaporation.

The two components are then combined after their appropriate aging cycles into one larger container. This mixture is stirred to ensure proper combination of the two constituents described elsewhere.¹⁷ The two individual sols are clear in color and devoid of emulsion before combination. After mixing, the solution becomes a mild yellow color. This yellow color will not affect the final coating due to the extremely thin nature of the coating.

B. Dipping procedure

The aged sols, both silica and titania, were tested individually on fused silica glass slides. The film consistencies were confirmed through both visual observation and optical microscope. The solutions were viewed for consistency and confirmed to be free of particulates or premature gelation. Further confirmation was achieved by a test coating to observe any visible imperfections. After the verification of ac-

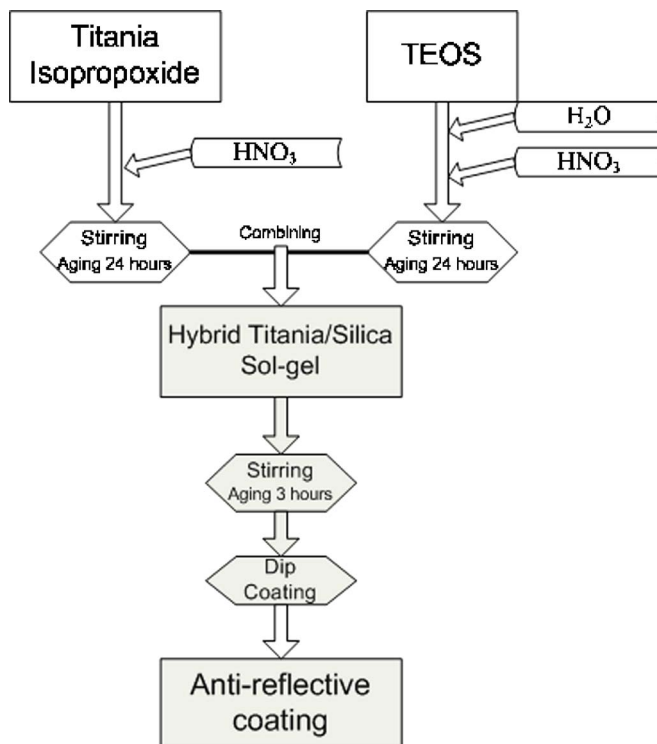


FIG. 1. Shown is a flow chart of the steps necessary to create the hybrid sol-gel. The two sol-gels are prepared and aged separately before mixing them.

ceptable aging times was completed, the two sols were mixed and stirred. The coating was done promptly following mixing to avoid gelation. The coatings done on chalcogenide glass were carried out in room temperature conditions.

A dip coating instrument (KSV Instruments Ltd., dip coater) was used to control vibrational effects and to increase the homogeneity of the film thickness. The rate used for withdrawal was 85 cm/min. At this rate, inconsistencies due to vibration were avoided. For coating the glass slides the instrument was equipped with a standard gripping mechanism. However, for the chalcogenide glass, of circular design, nearly 0.5 cm thick, it was necessary to fashion a holding ring of platinum wire. The glass slides and chalcogenide glass samples were cleaned prior to dipping in order to ensure a consistent coating surface.

C. Techniques used

Important aspects of sol-gels are commonly particle size, pH, and refractive index. These were analyzed for both of the elements of the hybrid sol-gel and of the hybrid in its combined form itself.

The particle size measurements were done on the Zeta-sizer (Malvern Instruments-Nano-series with cell type DTS0012 disposable sizing curvette). The dispersant chosen was a 2-propanol with viscosity 2.400 cP and a refractive index of 1.377 at a temperature of 25 °C.

The pH measurements were taken on a Denver Instruments (model 250 pH-ISE-conductivity meter). This instrument has a pH resolution of 0.001. Calibration was done

using pH buffer solutions from Fischer Chemicals of pH 4, 7, and 10. Automatic checks of the electrode are built into this system.

The surface chemistry of the silica-titania hybrid was studied using the x-ray photoelectron spectroscopy (XPS) utilizing PHI ESCA spectrometer (model 5400, Perkin-Elmer, Minnesota, having energy resolution of ± 0.1 eV, at a base pressure of 5×10^{-9} Torr using Mg $K\alpha$ radiation (1253.6 eV). The x-ray power during the analysis was 300 W. Both the survey and the high resolution narrow scan spectra were recorded at the pass energies of 44.75 and 35.75 eV, respectively, to achieve the maximum spectral resolution. The binding energy (BE) of the Au $4f_{7/2}$ at 84.0 ± 0.1 eV was used to calibrate the BE scale of the spectrometer. Any charging shifts produced by the samples were carefully corrected using the C (1s) BE level of 284.6 eV in the adventitious carbon.¹⁸

A Fourier transform infrared (FTIR-Spectrum One system, having wavelength range of $7800\text{--}350\text{ cm}^{-1}$ with KBr beam splitter) was utilized for the measurement of the transmission spectra over the desired wavelength of 1.5 to 5 μm . The resolution of the system is 0.5 cm^{-1} with a wave number accuracy of 0.1 cm^{-1} at 1600 cm^{-1} . The FTIR was used to measure the transmission of the bare and coated chalcogenide glass samples. The alignment of the sample was guaranteed through an alignment board and complimentary screw inserted sample holder. All measurements were reproduced multiple times to verify results obtained.

III. RESULTS AND DISCUSSION

A. Particle size, pH, and refractive index

Commonly found with silica derived sol-gels are particle sizes that are approximately 50 nm.⁴ In many cases, it is beneficial to create a less dense film, for the purposes of increasing transmission at the sacrifice of mechanical properties. Chalcogenide lenses may not be thermally stable,¹⁹ also having low resistance to abrasion which could affect the transmission quality of the glass. The sol-gel method can significantly enhance the abrasion resistance of the chalcogenide.²⁰ The size distribution ranges from a large number of particles at an average of 4–6 nm and a smaller amount of larger particles at an average of 150 nm (Fig. 2). The sol pH, along with composition and preparation, can alter the size of the particles within the sol. The silica sol was extremely acidic, at a pH of approximately 1. This was then offset by the neutral nature of the titania sol, pH of approximately 7, in the hybrid sol. The final pH of the hybrid sol was ~ 5 . In a pure silica system it has been determined that a lower pH, approximately 2.5 or lower, indicates growth towards linear chains, thereby forming a denser film, moving away from particles.²¹ In the opposite case at a pH of 7.5 or above, the particles are spherical creating a very porous film.²¹

As mentioned previously, the refractive index is an important part of an AR coating. In specific, it is one of the major difficulties in creating AR coatings for chalcogenides. Chal-

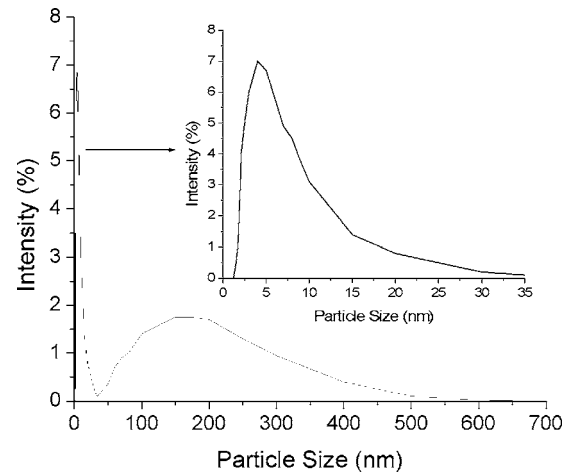


FIG. 2. Silica particle sizes shown are in two main ranges, between 2–10 nm and $\sim 100\text{--}200$ nm.

cogenides are known for their high refractive indices.¹ In this case, the chalcogenide used had a refractive index close to 2.55 at 3 μm . The base transmission of an uncoated sample can be calculated from the Fresnel²² formula using $n_s=2.55$ for the substrate and $n_m=1.0$ for air, the base reflectance at one side is

$$R = \left(\frac{n_s - n_m}{n_s + n_m} \right)^2 = \left[\frac{(n_s/n_m) - 1}{(n_s/n_m) + 1} \right]^2 = 0.1906.$$

This is then doubled for both sides to give a total of 38.9% reflectance or 61.9% transmission, which is verified experimentally. Further, focusing on a refractive index of 2.55, the closest approximation of the glass index of refraction averaging out dispersion effects, an attempt was made to fine tune a sol-gel blend to the aforementioned square root refractive index value of ~ 1.60 . This value is derived from the Fresnel formula and is a specific case where the reflection from the air-coating interface is assumed to be equal to the coating-substrate interface.²² Using the form

$$\frac{n_2 - n_1}{n_2 + n_1} = \frac{n_3 - n_2}{n_3 + n_2},$$

this reduces to

$$n_2 = \sqrt{n_3},$$

when $n_1=1$ using the air as the medium of the system. Using $n_1=1.0$ for air and $n_2=1.60$ for the coating, and $n_3=2.55$ for the chalcogenide substrate. The optimal refractive index for maximum transmission is found to be 1.60. This number does not take into account surface roughness, coating inconsistencies, or thickness variations.

In order to create such a refractive index, two solutions of known refractive index were combined to effectively average to the appropriate refractive index. The silica sol-gel coating, as prepared, has a known refractive index of ~ 1.3 and the second solution, titania sol-gel coating, as prepared, has a

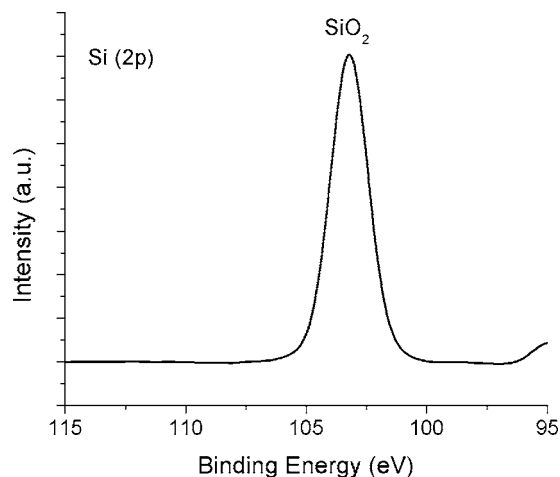


FIG. 3. XPS Si (2p) spectrum showing the SiO₂ formation. The peak is centered at 103.2 eV indicating the presence of SiO₂. No other peaks are present indicating that all of the silicon is in this form.

known refractive index of ~ 1.9 .^{4,6,23} The combination of the two is approximately an average of the two, based on the amount of each solution.¹⁶

B. Surface chemistry of the hybrid coating

XPS broad scan spectrum for the hybrid sol-gel showed the presence of O, Si, and Ti as expected. Upon further analysis using narrow high resolution XPS scans were obtained for Si (2p) and Ti (2p), within the BE ranges of 95–115 eV (Fig. 3) and 444–474 eV (Fig. 4). After analysis of the Si (2p), a peak at 103.2 is identified as the gel form of SiO₂. The presence of SiO₂ and TiO₂ is confirmed with the O (1s) peak (Fig. 5). Through heat treatments commonly used the OH⁻ species can be removed, increasing porosity and lowering RI.²⁴ The presence of the OH⁻ species did not affect coating properties. Similar heat treatments are usually performed on the titania sol-gel coatings, mainly used to create a crystalline structure.²⁴ The basic drying procedure in-

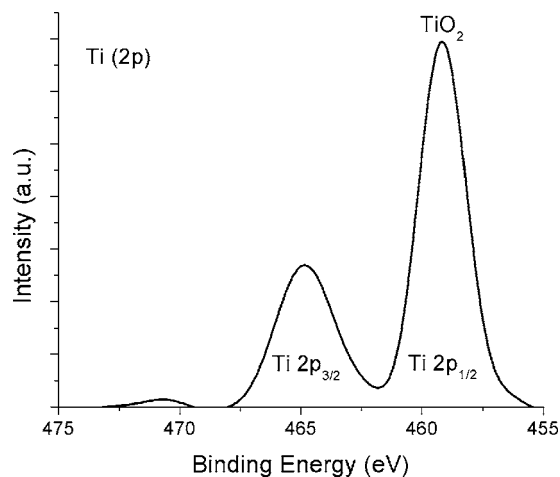


FIG. 4. XPS Ti (2p) showing the formation of TiO₂. The peak is centered at a binding energy of 459.16 eV signifying the presence of TiO₂. No other peaks are present indicating that all of the titanium is in this form.

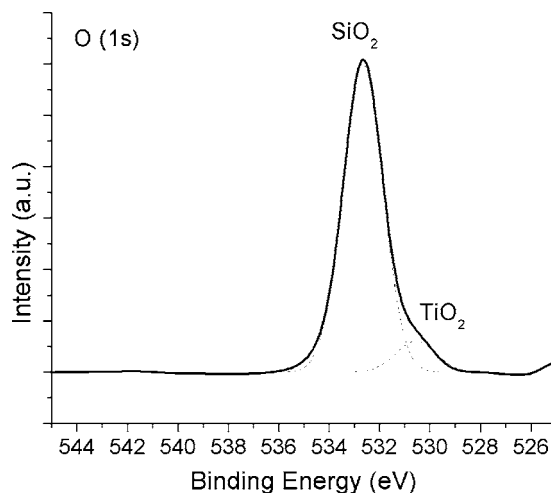


FIG. 5. XPS O (1s) showing the formation of SiO₂ and TiO₂. The SiO₂ peak is centered at a binding energy of 532.7 eV. The second peak, TiO₂, is located at 530.4 eV.

volves a heating at 100 °C in order to dry the coatings and then using increased heat, between 400 and 1000 °C, to achieve the desired crystallinity.⁷ However, in our coating system, the use of heat beyond 100 °C is not possible leaving the TiO₂ in the noncrystalline or amorphous phase. The Ti (2p) peak shows the amorphous nature of TiO₂ with a peak at 459.2 eV.

The increasing porosity with an increase of temperature of thermal treatment of the silica portion of the coating would typically be a useful method of lowering the RI and thereby increasing the anti-reflective quality of the silica coating. The titania portion of the coating is used solely for its RI value upon the combination of the two. The hybrid coating used in the present research uses the particular RI of silica which is 1.25, and any decrease in RI due to thermal treatment above 100 °C would be due to the detriment of the coating, rather than advantage. Also, the titania portion of the coating is more porous in its noncrystalline form than after it has been thermally treated shown in literature during heat treatments whereby the titania is crystallized.⁷ This increased porosity lowers the RI to a value of 1.91. With the combination of the two sol-gels, as previously discussed, the RI of the hybrid can be set near 1.64. The analysis of the XPS narrow scan spectra confirmed the formation of silica and titania chemical compounds in the hybrid sol-gel coating.

C. Transmission

A main focus of this research was to create a coating, sol-gel derived, that would aid in the maximum transmission of light at certain wavelengths of interest. Three such wavelengths, 1.5, 3.5, and 5 μm, were pursued for their particular benefits. These three wavelengths represent well used wavelengths of the near infrared region. Some common applications such as low cost optics by molding of chalcogenide glass,⁷ photodarkening,²⁵ or the use of chalcogenides for mi-

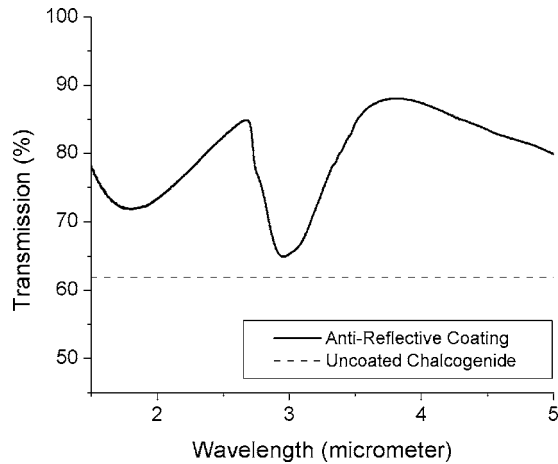


FIG. 6. Hybrid antireflective coating as compared to the transmission of the uncoated chalcogenide substrate.

crobiological function were used in early tumor diagnosis with the aid of specialized sensors capable of recording infrared signals of biomolecules.²⁶

In the present research, the original transmission in the range of 1.5–5 μm wavelengths is 61.9%. As shown in Fig. 6, the coating enhances the transmission at the first key wavelength of 1.5 μm to 78%. In the middle area of 3 μm there is a dip in transmission due to absorbance of the light due to residual water in the coating. At the next wavelength of interest, 3.5 μm , the increase is very significant. The matching of the substrate and the film is much better here, increasing transmission 22.6%, yielding 84.5% total transmission. In comparison, a typical fused silica glass system with a base transmission of $\sim 90\%$ is increased to a coating with a final transmission of 99.5% at one particular wavelength and an average that seems closer to 94%.⁴ The increase in the fused silica glass system even at its highest point was only 9%, giving perspective to the incredible 22.6% increase shown in the chalcogenide system. Due to the higher strength requirements of a single coating, prepared presently, the transmission will be sacrificed slightly. Finally, at the wavelength of interest, 5 μm , we see another great increase in transmission from the original. With an increase of 18% at this wavelength from the original 61.9%, there is a substantial increase in transmission. An overview of this transmission increase has been shown in Fig. 7.

The ability of a coating to perform within one week of its original creation is an important step in the development of a successful coating. However, it is more relevant to view the functioning of a coating several weeks after its initial application and testing. It is the intrinsic nature of a sol-gel to relax over time, slowly releasing the remaining moisture and solidifying further. The first step towards aging is denoted as polymerization and represented by the condensation reaction $\equiv\text{Si}-\text{OH}+\text{HO}-\text{Si}\equiv\rightarrow\equiv\text{Si}-\text{O}-\text{Si}\equiv+\text{H}_2\text{O}$ which links up the initial network.²⁷ Following polymerization, hydrolysis occurs which further strengthens the network. Hydrolysis is shown here by the reaction $\equiv\text{Si}-\text{OR}+\text{H}_2\text{O}\rightarrow\equiv\text{Si}-\text{OH}+\text{ROH}$.²⁶ This reaction is reversible, but with the presence of

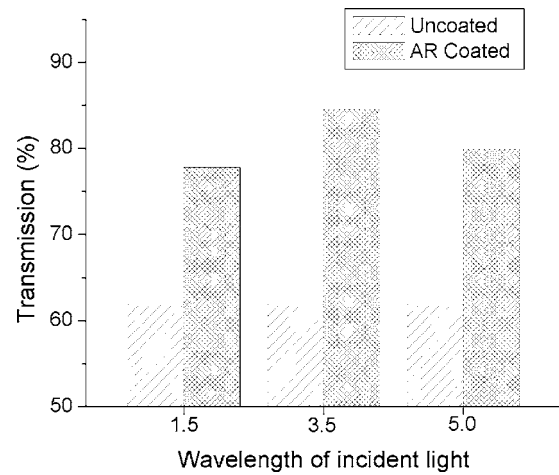


FIG. 7. Overview of the gains in transmission at particular wavelengths, 1.5, 3.5, and 5.0 μm .

enough water, it can be encouraged to not reverse. This continues until such time as the coating is in equilibrium with its surroundings and the substrate. The relaxation of the film with aging presumably involves densification and thinning of the film.²⁸ The densification process is mediated by bond cleavage due to the movement of electrons from the valence band to the conduction.²⁷ The movement leads to the rearrangement of the gel network through the condensation reaction which causes densification. This densification changes the phase cancellation properties of the reflected waves, affected each of the wavelengths differently. The dip in the transmission spectra is due to the absorption of solvent and water remaining in the coating. Typically heat treatments can minimize these effects, but we do not use heat treatments. This dip does not affect our areas of interest. This is the reason it remains.

IV. CONCLUSION

Chalcogenide glass has many important and far-reaching uses that will be fully explored in the future. Continued research will focus on harnessing the unique properties, those already known and those which can be further exploited. In order to use the chalcogenides intrinsic transmission in the infrared region to its fullest extent, it is essential to enhance the property through the addition of antireflective coatings. The coating material and method presented here is a low cost, room temperature venture that makes use of the unique properties of sol-gel, while drastically enhancing the transmission of chalcogenides in the near infrared region. The use of specific wavelengths and the creation of a coating for these wavelengths is a feature of this research. The creation of a coating that is a viable AR coating for chalcogenide glass at several wavelengths in the near infrared region is presented herein. This considerable gain in transmission, at points within the 1.5–5 μm range, is an important step forward in AR coatings and should prove to be of future interest as the applications of chalcogenides in this region are fully realized.

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